91602
new 82-10

COMPLIMENTARY COPY
Please Credit Ontario Hydro Research if
Reproduced in Whole or in Part

ontario hydro
research division

To: Dr. D. Mills
Director of Research
KR116

Oxygen Isotope Production Methods: Analysis of Available Techniques

Jeffrey R. Robins
Frank E. Bartoszek

Oxygen-18 is a valuable isotope for use in chemistry, physics and medicine. Its use is also expanding in human nutritional sciences and medical diagnostics. This report reviews 14 separation methods for this isotope and concludes that the distillation of light water is the best method for Ontario Hydro.

1. Introduction

Hydrogen and deuterium are not the only "life science" isotopes that find extensive use in chemistry, physics and medicine. The isotopes of carbon, nitrogen and oxygen are also separated and marketed for various applications. The stable isotopes of oxygen, ^{18}O, and to a lesser extent ^{17}O, are isotopes that are finding increased uses, especially in the areas of human nutritional sciences and medical diagnostics.

At the end of 1987, the Stable Isotope Group of New Business Ventures Division expressed an interest in the production of oxygen isotopes because measurements had shown that heavy water produced by the Bruce Heavy Water plant contained greater than 1% ^{18}O. Ordinary water contains about 0.2% ^{18}O. Water enriched in ^{18}O is required in certain medical diagnostics, and therefore there was a promise of sales of this material.

Heavy water is produced at the Bruce plant by a combination of chemical exchange and distillation. Distillation in the Finishing Units enriches the deuterium concentration from 30% to reactor grade heavy water, and coincindently enriches the oxygen-18 concentration. For part of 1988, the heavy water plant was scheduled for a shut down for maintenance. During this time we could use the Finishing Unit F2 for a series of tests on oxygen isotope enrichment by running the unit on total reflux using high grade heavy water as the feed /1/. By April, 1988 it was clear that the optimistic measurements of the oxygen concentration in the heavy water could not be confirmed. Rather than 1%, closer to 0.3% $D_2{}^{18}O$ was found for heavy water from the F2 finishing unit. We also found a wide variation from laboratory to laboratory in the measured value of ^{18}O in heavy water . Based on the known distillation characteristics of the unit and using a starting concentration of ~0.3% ^{18}O, a final concentration of ~1.75% $D_2{}^{18}O$ was predicted for the trial.

job	file	date	report no.
16-682	819.43	May 14, 1991	91-114-K

LEGAL NOTICE

This report was prepared by Ontario Hydro and, while effort has been made to assure the accuracy and applicability of the material contained herein, neither Ontario Hydro nor any person acting on its behalf:

(a) makes any warranty, express or implied with respect to the use of any information, apparatus, method or process disclosed in this report or that such use may not infringe privately owned rights; or

(b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

Despite this fairly low final concentration, the trial continued and on August 22 the unit was charged with 99+% D_2O and started on total reflux. By October 17 the concentration had reached 1.26 % ^{18}O and the operation staff began removing product. Unfortunately a steam failure occurred on that date and the isotopic gradient was lost within the unit and the trial terminated.

The trial showed the capabilities and the limitations of the finishing unit at Bruce. After this trial, a study was initiated to assess possible methods of isotope separation for oxygen. This study was part of the Stable Isotope Research program at Research Division. The objective was to determine the best choice for a production facility for oxygen-18 for Ontario Hydro.

2. Isotope Separation Techniques Studied

Eighteen separation methods were studied, including methods used commercially to produce these isotopes, methods that are still being developed, and the continued operation of equipment at BHWP. These isotope separation methods are given in Table 1.

TABLE 1.
Oxygen Isotope Separation Techniques Evaluated

Fully Developed	Under Development	Using Existing Equipment
NO Distillation	Laser Isotope Separation	Operation of the F2 Finishing Unit at BHWP using D_2O as a feedstock
H_2O Distillation	Distillation of the NO/CH_4 Azeotrope	
CO Distillation	Chemical Exchange Systems involving Carbamates and Amines	
O_2 Distillation	GC Separation and Selective Absorption on Substrates	
NO / H_2O / HNO_3 Chemical Exchange	Magnetic Isotope Separation	
CO_2 / H_2O Chemical Exchange	Thermal Diffusion of CO	
Thermal Diffusion of O_2		

3. Criteria Used for Comparison

The fully developed separation methods were evaluated using 14 criteria. These were chosen to give a clear picture of each method. The criteria are listed in Table 2.

TABLE 2.
Technical Areas Evaluated for Each Isotope Separation Technique

1. Method	a description of the isotope separation method; this also includes a value for α, the single stage separation constant, and the natural abundance of the various isotopic species.
2. Equipment	a description of the equipment needed, especially any specialized equipment.
3. Feed stock	feed materials, and some of their properties.
4. Product	isotope containing products produced by the process and whether they can be marketed directly, or have to be converted to some other material.
5. Other chemicals	other process materials needed in large quantities.
6. Difficulty of operation / degree of complexity	comments on any potential problems with the process that will increase the complexity of operation.
7. Reliability / scale of process / external experience	external experience with this process and whether or not it has been used on a large scale.
8. Internal experience	relevant Ontario Hydro experience with the process or techniques used.
9. Size restrictions on the process	any known sizing problems with the process.
10. Analysis systems required	analytical systems required to monitor the operation of the unit and whether they are currently available at Ontario Hydro.
11. Waste disposal	other materials produced along with the isotope-containing product.
12. Safety	safety problems to be considered in operating the process.
13. Interest at Hydro	interest within Ontario Hydro for this process apart from production of ^{18}O.
14. Other notes	comments on the process, especially notes on its possible use for ^{17}O.

Each of the separation techniques studied is discussed under the above criteria in the appendices of this report.

4. Evaluation

Each of the methods reviewed were qualitatively assessed according to the criteria listed, by numerically ranking each category from 1 to 8, with 8 being the best condition in that category and 1 the worst. For example, the safest production method ranks 8 and the least safe ranks 1. The methods with the highest totals within the ranking system were considered for further examination.

Each of the above criteria has equal weight and the ranking was done with the intention of finding the best match for Ontario Hydro. The results of the ranking are given in Table 3.

TABLE 3.
Ranking of the Various Methods[1]

	NO Distillation	H_2O Distillation	CO Distillation	O_2 Distillation	$NO/NO_2/HNO_2$ Chemical Exchange	CO_2/H_2O Chemical Exchange	Thermal Diffusion of O_2	Operation of the F2 finishing Unit
Method	8	4	5	1	7	6	2	4
Equipment	2	6	4	3	1	5	7	8
Feed Stock	2	8	6	3	3	6	4	8
Product	2	8	5	4	1	5	4	8
Other Chemicals	2	8	4	5	1	3	7	8
Difficulty	3	8	5	3	1	2	7	5
Reliability/ Scale/ External Experience	8	6	7	2	5	4	1	3
OH Experience	3	7	4	6	1	5	1	8
Size of Production	7	8	7	7	4	2	1	7
Analysis Systems	2	7	6	5	1	3	5	7
Waste	5	7	3	5	1	2	8	7
Safety	1	8	4	3	3	5	3	8
Interest at Hydro	5	8	7	4	1	2	6	8
TOTAL	50	93	62	51	30	50	56	89
RANKING	7	1	3	5	8	6	4	2

[1] Numerical ranking in each category from 1 to 8, with 8 being the best condition in that category and 1 the worst. Each criteria has equal weighting.

Conclusion

The four best methods for oxygen isotope production were selected for further evaluation:

- H_2O Distillation
- Operation of the F2 Finishing Unit (using heavy water)
- CO Distillation
- Thermal Diffusion of O_2

These were further examined using the following:

- the potential size of the ^{18}O market
- the market demands in terms of production volume, product purity, and type of product
- the state of the final product from the process and whether it needs further processing
- a rough estimate of production costs.

Market studies for oxygen-18 were commissioned in the middle of 1989. The initial evaluation indicated that the market was relatively flat. There are only two producers of oxygen isotopes in the West and both were expanding their production facilities. Subsequent study showed a possibility for growth that could exceed even the expanded production capability. This growth was expected from adoption of PET (Positron Emission Tomography) scanning as a clinical diagnostic procedure. The development of this procedure could lead to an oxygen-18 demand of approximately 100 kg/a. We therefore decided that a good reference size for Ontario Hydro to develop would be a 40 kg/a plant producing 99 % ^{18}O.

The method that best fit all the criteria and the market conditions is a plant based on the distillation of light water.

Further developments of this method were undertaken by the Nuclear Systems and Integration Section of Nuclear Engineering Department. A conceptual design for a plant /2/ producing 40 kg/a of 99% $H_2{}^{18}O$ was issued at the end of 1990.

Approved:

A.F. Baljet
Manager
Electrical Research Department

Submitted:

J.R. Robins
Engineer/Scientist
Science Section

Reviewed:

for
F. Chu
Section Head
Science Section

F.E. Bartoszek
Engineer/Scientist
Science Section

References

1. Handbury J. "Finishing Unit No. 2 - Oxygen 18 Trial Report", Bruce Heavy Water Plant, Report No. TG-7-90, (1990).

2. Busigin A., Kalyanam K.M., "Conceptual Design of an Oxygen-18 Production Facility Based on Water Distillation", Nuclear Engineering Department Report No. 90037, (1990).

Appendix 1.
NO Distillation

1. Method

Cryogenic distillation of nitric oxide (NO) at 121 K (-152 C) in a packed column at atmospheric pressure. Production of ^{15}N and ^{18}O is possible. There are 5 isotopes present giving a total of 6 molecular species:

Species	Abundance	Separation Factor (α)
$^{14}N^{16}O$	99.395%	----------
$^{15}N^{16}O$	0.364%	1.0270
$^{14}N^{18}O$	0.203%	1.0372
$^{14}N^{17}O$	0.037%	1.0186
$^{15}N^{18}O$	7.45 ppm	1.0642
$^{15}N^{17}O$	1.35 ppm	1.0456

2. Equipment

- cryogenic distillation columns, stainless steel packing
- columns insulated with aluminized Mylar within a high vacuum jacket
- operating temperature of 121 K, using liquid nitrogen as a primary refrigerant and liquid oxygen at ≈ 11 atmospheres as a secondary refrigerant
- vacuum systems to maintain the insulation for the columns
- control systems for the cryogenics and gas handling for the feed, waste, and product streams.
- gas purification plant operating at 77 K to remove N_2 and NO_2 and a short pre-column to remove N_2O from commercial nitric oxide
- because of the difficulty of obtaining NO an on-site production facility for nitric oxide may be necessary using nitric acid as a feed and reacting it with SO_2 producing H_2SO_4 as a by-product

3. Feed stock

NO, nitric oxide - colourless, moderately reactive, explosive, toxic gas (toxic at the ppm level). It reacts immediately with oxygen to form acrid, brown NO_2:

$$2NO + O_2 \rightarrow 2NO_2$$

NO is only slightly corrosive, NO_2 is very corrosive. At high pressures and moderate temperatures (≈50 C) NO rapidly disproportionates

$$3NO \rightarrow N_2O + NO_2$$

NO is not readily available in large quantities.

4. Product

The final product is enriched NO with reported enrichments as high as 8.3% ^{17}O, 98.2% ^{18}O and 93.9% ^{15}N. The marketable product is $H_2{}^{18}O$, which can be produced from the reaction with hydrogen gas, ie

$$2NO + H_2 \rightarrow 2H_2O + N_2$$

5. Other chemicals

Liquid nitrogen, liquid oxygen, hydrogen gas, possibly SO_2

6. Difficulty / complexity

Gas handling is difficult because NO is toxic and the impurities are corrosive. Gas monitoring is necessary. There is an explosion hazard. The distillation process requires isotope equilibration outside the column. [2]

7. Reliability / scale / external experience

Because of the large separation factors (α) and because both ^{15}N and ^{18}O are produced this is the method of choice for commercial production. Los Alamos and Isotec have NO distillation columns operating. Los Alamos has worked in this area since early 1960. Both companies operate large stills.

8. Internal Experience

- cryogenic distillation - extensive experience
- NO handling - no experience

9. Size of production

- no major restrictions on size.
- process uses long, small diameter columns, usually in groups.
- refrigeration load increases with increase in size.

10. Analysis systems required

Mass spectrometric analysis of NO is complicated. The 6 molecular species give only 4 mass peaks between masses 30 and 33. Los Alamos uses spark discharge in NO to form N_2 and O_2, with N_2 giving peaks at 28, 29 and 30,and O_2 giving peaks at 32, 33, 34, 35 and 36. This data provides atomic abundances, but no information on the molecular abundances of NO. Similar spark discharge equipment is not available at Hydro.

11. Waste disposal

Waste NO gas is both toxic and expensive. Large scale separation plant would return this waste gas to the original supplier as a purified product.

---

[2] In isotopic equilibration, molecules react over a catalyst at elevated temperatures and then pass back to the column. A simple example occurs in the distillation of hydrogen where HD concentrates at the bottom of the column. However, 100 % HD is only 50% pure deuterium. Reaction of the gas over platinum at 300 °C breaks the HD apart and it reforms as an equilibrium mixture of H_2, D_2, and HD. This mixture returns to the column to yield pure D_2 at the bottom of the column. These types of equilibration steps are used in a number of isotope separation schemes.

12. Safety concerns

Because NO is toxic, corrosive, and explosive, it requires monitoring. One of Los Alamos's cryogenic stills exploded in the upper section (the actual column is underground). The present column is inside a concrete labyrinth in a building with double walls.

13. Interest at Hydro

Little interest in this process.

14. Other notes

Los Alamos recently had to remove their column from the ground because a copper pipe feeding into the boiler corroded.

References

1. McInteer B.B., Potter R.M., "Nitric Oxide Distillation Plant for Isotope Separation", I&EC Process Design and Development, *4(1)*, 35-42, 1965.

Appendix 2.
H_2O Distillation

1. Method

Low temperature (≈ 60 C), low pressure (sub atmospheric) distillation of water in packed columns. Concentration of both D and ^{18}O occur. The species present are as follows:

Species	Abundance	Separation Factor (α)
$H_2{}^{16}O$	99.774%	----------
$H_2{}^{18}O$	0.189%	1.0081
$H_2{}^{17}O$	0.037%	1.0043
$D_2{}^{18}O$	------	1.0070

2. Equipment

- distillation columns packed with phosphor-bronze packing (Goodloe or Sulzer) that has an oxide coating to improve wetting.
- vacuum system to maintain the column pressure below atmospheric.
- a falling film evaporator or at least a specially designed boiler to boil water smoothly.

3. Feed stock

light water

4. Product

$D_2{}^{18}O$ 95+ atom%, $D_2{}^{17}O$ 1 - 2 atom%; both are directly marketable. However, for many medical uses such as nutritional studies, the water must be normalized, i.e. the deuterium exchanged for hydrogen to produce $H_2{}^{18}O$.

5. Other chemicals

none

6. Difficulty / complexity

A large number of theoretical plates are required for this separation (>5000). The columns are easy to operate: external isotope equilibration stages are required because the necessary isotopic scrambling process goes on inside the column naturally. Some systems that enrich ^{18}O remove water part way through to replace the deuterium with hydrogen because the separation is a slightly better for H_2O. Replacing deuterium with hydrogen is necessary if enough plates are built into the towers.

7. Reliability / scale / external experience

Large scale, reliable, water distillation systems are in operation around the world. Despite the poor separation factor, this method is currently in use at the Weizmann Institute in Israel and has been used at Karlsruhe in Germany and at Oak Ridge to produce ^{18}O.

8. Internal Experience

Hydro has the world's best experience in isotope separation using water distillation. This experience includes experimental design, theory, engineering, and operations.

9. Size of production

No limit

10. Analysis systems

Mass spectrometric analysis of H_2O for ^{18}O is well known. Measurements are made by equilibrating CO_2 with the water, since water is a poor material to put in a mass spectrometer. The necessary mass spectrometer is available at the Research Division, but the CO_2 equilibration system must be built. New methods using diode lasers to measure ^{18}O are under development at a number of research organizations.

11. Waste disposal

none

12. Safety

No major hazards exist. Safety methods duplicate those used at the finishing units at the BHWP.

13. Interest at Hydro

NMMD would like to test a packing other than Sulzer packing for water distillation. CFFTP is also interested in tests of "small scale" water distillation systems as a tool for HTO cleanup.

14. Other notes

The production of ^{17}O is difficult using this process because oxygen-17 is a "middle isotope" and concentrates in the centre sections of the distillation columns rather than at the ends. Therefore oxygen-17 production requires a small side stream to be removed from the columns, and enriched separately.

References

1. Staschewski D., "Production of Oxygen-18 and Oxygen-17 by Countercurrent Distillation of Reactor-Grade Heavy Water", Stable Isotopes in the Life Sciences, IAEA, (1977).

2. Wolf D., Cohen H., "Process Design Considerations and Steady-State Operational Data for the Separation of Isotopes of Oxygen", Can. J. of Chem. Eng., 50, 621 (1972).

Appendix 3.
CO Distillation

1. Method

Cryogenic distillation of carbon monoxide (CO) at 68 K (-205 C) in a packed column at or below atmospheric pressure. There are 5 atomic species giving a total of 6 molecular species:

Species	Abundance	Separation Factor (α)
$^{12}C^{16}O$	98.65%	---------
$^{13}C^{16}O$	1.105%	1.011
$^{12}C^{18}O$	0.202%	1.0068
$^{12}C^{17}O$	0.0366%	1.0036
$^{13}C^{18}O$	22.6 ppm	1.018
$^{13}C^{17}O$	4.1 ppm	1.015

2. Equipment

- cryogenic distillation columns packed with a stainless steel packing
- operates at or below atmospheric pressure
- liquid nitrogen as a refrigerant at either atmospheric or reduced pressure (depending on the operating temperature)
- vacuum insulated columns
- vacuum systems for the liquid nitrogen and for the insulation
- control systems for the cryogenics, and for gas handling (feed, waste and product streams).

3. Feed stock

CO - carbon monoxide, a colourless, odourless, noncorrosive, toxic gas available in large quantities.

4. Product

Enriched $^{12}C^{18}O$, and possibly some $^{12}C^{17}O$ at low levels of enrichment. However, the market requires the oxygen-18 in water. This exchange could be done over a nickel catalyst with hydrogen gas:

$$C^{18}O + 3H_2 \rightarrow H_2{}^{18}O + CH_4$$

5. Other chemicals

liquid nitrogen, hydrogen gas

6. Difficulty / complexity

The apparatus requires only one refrigerant, liquid nitrogen. Reducing the pressure, and hence temperature, of the liquid nitrogen improves the separation efficiency. There is no explosion hazard or corrosion problems with liquid nitrogen or liquid CO. Because CO is toxic, however, the system must be monitored for this gas. The distillation also requires some stages of isotopic equilibration outside the column.

7. Reliability / scale / external experience

This method has not been used extensively to produce oxygen isotopes. However large systems using this method to separate ^{13}C have been operated at Los Alamos, Cambridge Isotopes, and Isotec. The distillation systems at Los Alamos have operated continuously for many years.

8. Internal experience

Cryogenic distillation of CO to develop a ^{14}C separation system has operated continuously, at lab scale, at Research Division for over 4 years. Work continues in our laboratory to study ^{14}C separation on a pilot plant scale. A large scale ^{14}C pilot plant is being designed.

9. Size

No limit known

10. Analysis system

The isotopes can be measured directly using mass spectrometry of CO. Research Division has a mass spectrometer to measure $^{13}C/^{12}C$ ratios. This instrument can also measure oxygen isotopes.

11. Waste disposal

- disposal of CO gas
- large scale operations could sell CO back to the supplier as purified gas.

12. Safety

- CO is a toxic gas and requires monitoring.
- standard safety procedures for handling cryogenic materials.

13. Interest at Hydro

Research Division and other groups are interested in ^{14}C separation using cryogenic distillation of CO.

14. Other notes

This technique also offers a method of enriching ^{17}O by drawing off a side stream and distilling this material in a small set of columns installed along side the ^{14}C pilot plant.

References

1. Johns T.F., Kronberger H., London H., "Preparation of Standard Gases - Enrichment of the Heavy Isotopes of Carbon and Oxygen by Fractional Distillation of Carbon Monoxide", Mass Spectrometry A Report of the Conference of the Institute of Petroleum, Manchester (1950).

2. McInteer B.B., "Isotope Separation by Distillation: Design of a Carbon-13 Plant", Sep. Science & Tech., 15(3), 491 (1980).

Appendix 4.
O_2 Distillation

1. Method

Cryogenic distillation of oxygen (O_2) in a packed column at 70 K (-203 C), below atmospheric pressure. There are 3 isotopes and a total of 6 molecular species:

Species	Abundance	Separation Factor (α)
$^{16}O^{16}O$	99.518%	----------
$^{16}O^{18}O$	0.188%	1.0103
$^{16}O^{17}O$	0.037%	?
$^{18}O^{18}O$	3.57 ppm	?
$^{17}O^{18}O$	0.7 ppm	?
$^{17}O^{17}O$	0.14 ppm	?

2. Equipment

- packed column distillation using stainless steel packing; the distillation system is identical to that used for CO distillation.
- liquid nitrogen refrigerant at reduced pressure.
- the equipment rated for oxygen service; no grease or oil used in the system.

3. Feed stock

O_2 - oxygen, a colourless, reactive gas that supports combustion.

4. Product

Enriched oxygen gas, probably in the form $^{16}O^{18}O$, could be marketed directly. However, to simplify handing and to meet other market demands, this product could be converted to water using precious metal catalysts and hydrogen gas. Any design however, must avoid explosive mixtures of oxygen and hydrogen.

5. Other chemicals

liquid nitrogen

6. Difficulty / complexity

- equipment rated for liquid oxygen service.
- the distillation requires isotopic equilibration outside the column
- not all the separation constants are known and they must be determined.

7. Reliability / scale / external experience

This method has been used to manufacture 25% purity material on a small scale by Prochem (British Oxygen). Liquid oxygen is handled routinely in large quantity in the liquid air business.

8. Internal experience

Experience with cryogenic distillation at these temperatures.

9. Size

Unknown but liquid oxygen plants exist in large scale

10. Analysis systems

Mass spectrometry of oxygen. No experience with such analysis at Research Division, but the necessary mass spectrometer exists.

11. Waste disposal

none

12. Safety

Handling large quantities of liquid oxygen.

13. Interest at Hydro

Little interest in this process

14. Other notes

References

1. Edmunds A.O., Lockhart J.M., "Separation of Stable Isotopes and the Preparation of Labelled compounds with Special Reference to ^{13}C, ^{15}N, and ^{18}O", IAEA-SM-191/7.

2. Groth W., Ihle H., Murrenhoff A., "Bestimmung des Dampfdruckverhältnisses ^{16}O ^{16}O/ ^{18}O ^{18}O zwischen 63K und 74K", Angew. Chem., 68, 644 (1956).

Appendix 5.
$NO/H_2O/HNO_3$ Chemical Exchange

1. Method

- chemical exchange between NO(g) and 6 to 8M HNO_3(liq) at room temperature.
- the reaction enriches ^{15}N in the liquid phase and ^{18}O in the gas phase.

^{15}N: $^{15}NO(g) + H^{14}NO_3(liq) \rightleftharpoons {}^{14}NO(g) + H^{15}NO_3(liq)$ $\alpha = 1.055$ (25 C)

^{18}O: $N^{16}O(g) + H_2{}^{18}O(liq) \rightleftharpoons N^{18}O(g) + H_2{}^{16}O(liq)$ $\alpha = 1.020$ (25 C)

2. Equipment

The chemical exchange process (see Figure 1) consists of two systems linked together, one for nitrogen-15 and one for oxygen-18. For nitrogen-15 separation, HNO_3 enters the top of the separation column where it equilibrates with a countercurrent stream of NO. The NO for this stream is produced within the unit by reacting the HNO_3, that leaves the separation column with SO_2, i.e.

$$2HNO_3 + 3SO_2 + 2H_2O \rightleftharpoons 3H_2SO_4 + 2NO(g)$$

A small side stream of HNO_3 from the bottom of the column provides the product, $H^{15}NO_3$. The reaction to form NO uses SO_2 as feed and produces H_2SO_4 as a byproduct. Nitric oxide leaving the top of the separation column is depleted in nitrogen-15.

Oxygen-18 is produced in the second system, which uses the waste NO from the nitrogen-15 system, to equilibrate with an H_2O - HNO_3 solution. Oxygen-18 collects in the NO which is removed as product at the top of the separation tower. Reflux - - consisting of the H_2O - HNO_3 solution - - is produced by passing the remaining NO through an electric discharge to produce N_2 and O_2. The oxygen reacts with excess NO to produce NO_2. The rest of the NO stream reacts with H_2 to form water. This water is mixed with the NO_2 to form HNO_3 reflux. Ammonia is also formed and this must be trapped, decomposed and any water formed captured and returned.

3. Feed stock

- NO, nitric oxide - a colourless, moderately reactive, explosive, toxic gas (toxic at the ppm level).
- HNO_3, nitric acid - a strong, corrosive acid.

4. Product

- ^{15}N is obtained at the bottom of the column as HNO_3.
- ^{18}O is obtained at the top of the column series as NO gas.
- products require further treatment before marketing.

5. Other chemicals

SO_2 and H_2SO_4 at the bottom of the column, H_2 at the top.

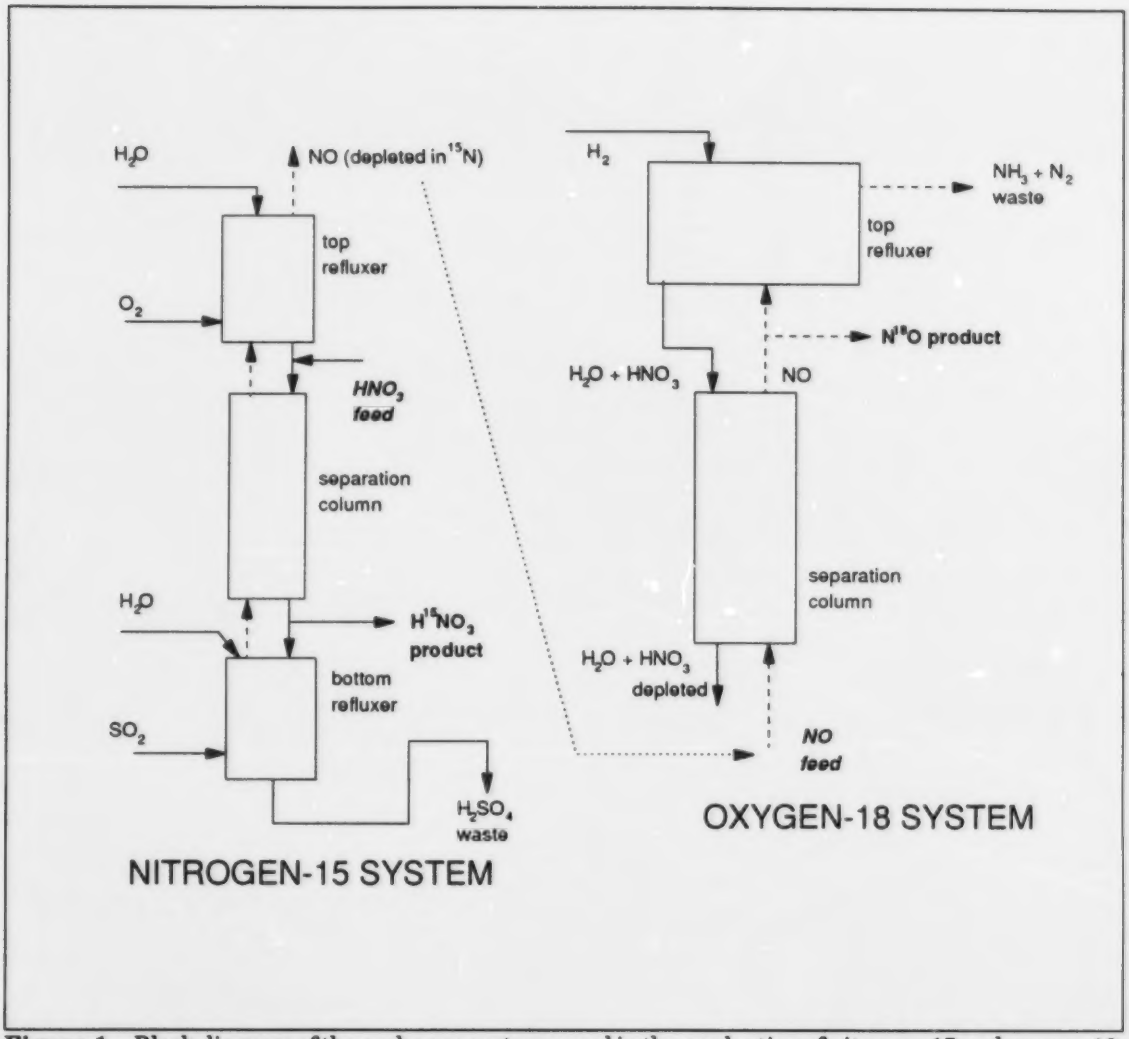

Figure 1. Block diagram of the exchange systems used in the production of nitrogen-15 and oxygen-18.

6. Difficulty / complexity

- construction materials compatible with corrosive gas and liquid streams
- pumps handle 6 - 8M HNO_3
- monitoring systems for NO
- top of the column system requires absorption devices to prevent loss of water vapour which contains product
- interconnections between columns are complex
- reflux systems on both the columns involve complex reactions.

7. Reliability / scale / external experience

- industrial scale plants have been built to extract ^{15}N in East Germany by the Central Institute for Isotope and Radiation Research, and in England by Prochem.
- dual oxygen/nitrogen system has been investigated by a group at Columbia University.
- Isotec used a chemical exchange process to produce these isotopes before their NO distillation system was operating.

8. Internal experience

none

9. Size

Industrial scale plants have been built; process should scale to any size.

10. Analysis systems

- mass spectrometric analysis is needed for the isotopes.
- chemical analysis needed to maintain the correct HNO_3 concentration.

11. Waste disposal

- H_2SO_4 is produced as a by-product in large quantities.
- NO, NO_2 and HNO_3 are wastes.

12. Safety

- two strong acids are involved, H_2SO_4 and HNO_3.
- NO is toxic
- NO_2 produced in the process is both toxic and corrosive.
- large quantities of hydrogen gas and sulphur dioxide gas are used.

13. Interest at Hydro

none

14. Other notes

Despite their apparent complexity, large scale chemical exchange systems have been operated, but they are best coupled to industrial systems that use all the chemicals produced.

References

1. Taylor T. I., "Chemical Exchange Reactions for the Concentration of Nitrogen and Oxygen Isotopes", J. de Chimie Physique et de Physia-chemie Biologique, 60, 155 (1963).

2. Saxena S. C., Taylor T. I., "Enrichment of Oxygen-18 by the Chemical Exchange of Nitric Acid Solutions", J. Phys. Chem.,66, 1480 (1962).

3. Krell E., Jonas C., "Industrial Plants for Production of Highly Enriched Nitrogen-15", Stable Isotopes in the Life Sciences, IAEA, 1977.

Appendix 6.
CO_2/H_2O Chemical Exchange

1. Method

- chemical exchange between carbon dioxide, CO_2 and water, H_2O
- at room temperature (or above) and moderate pressures (≈ 5 to 10 atmospheres).
- the ^{18}O collects in the gas stream:

$$C^{16}O_2(g) + H_2{}^{18}O(liq) \rightleftarrows C^{16}O^{18}O(g) + H_2{}^{16}O(liq) \qquad \alpha = 1.0412 \text{ (25 C)}$$

2. Equipment

The exchange is favourable but slow. The equilibration between water and carbon dioxide is the most common method for measuring ^{18}O on a mass spectrometer. For a single stage reaction at room temperature, the half reaction time is 42 minutes; 99% of equilibrium requires 4 hours and 37 minutes. The reaction relies on dissolving carbon dioxide in water followed by exchange:

$$CO_2(gas) \rightleftarrows CO_2(aq)$$

$$CO_2(aq) + H_2O \rightleftarrows HCO_3^- + H^+$$

The limiting step is dissolving carbon dioxide in water. Various techniques can increase the rate of dissolving CO_2, such as operation at high temperatures and pressures, or the addition of ammonia. The CO_2 leaving the top of the exchange tower must be mixed with hydrogen gas and passed over a hot nickel catalyst to form water for the reflux system:

$$CO_2 + 4H_2O \rightarrow 2H_2O + CH_4$$

3. Feed stock

CO_2, H_2O

4. Product

- enriched CO_2
- must be chemically modified to meet market demand (water).

5. Other chemicals

ammonia and hydrogen

6. Difficulty / complexity

Because of low solubility, the HETP varies from 15 to 200 cm (typical distillation values are 1 to 5 cm) which requires long towers to obtain significant enrichment. Addition of ammonia forms ammonium carbamate and ammonium bicarbonate, which are solids and tend to plug the system. The necessary isotopic purity cannot be achieved in one exchange column and interconnections between successive

columns are complex because of the CO_2 decomposition system used to provide reflux. Methane is also produced from this reaction.

7. Reliability / scale / external experience

- one exchange column using this principle was built as a university experiment in the early 1950s.
- no work has been done since.
- the exchange has a favourable α, but is limited by solubility.

8. Internal experience

Limited experience using CO_2/H_2O exchange for measuring ^{18}O on a mass spectrometer.

9. Size

- no information on any limitations to this process; current estimates of the HETP indicate a large plant is necessary.

10. Analysis systems

- mass spectrometric analysis for ^{18}O in CO_2.
- chemical analysis to control ammonia addition.

11. Waste disposal

- ammonia dissolved in water.
- methane gas
- some CO_2

12. Safety

hydrogen gas and ammonia are used in large quantities

13. Interest at Hydro

none

14. Other notes

Work required to solve the exchange problems.

References

1. Boyd W.T., White R.R., "Concentration of Oxygen 18 by Chemical Exchange", Ind. & Eng. Chem., 44, 2202 (1952).

2. Boyd W.T., "The Concentration of Oxygen 18 by Chemical Exchange", PhD thesis, University of Michigan, 1951.

Appendix 7.
Thermal Diffusion of O_2

1. Method

Thermal diffusion systems use an apparatus developed by Clusius and Dickel - - a long, vertical tube, cooled externally with a water jacket and heated internally by a hot wire filament on the axis of the tube. Thermal diffusion drives the lighter isotopes towards the hot surface, where they are carried upwards by convection. The heavier isotopes descend by convection near the cold surface. For oxygen, cold wall temperatures of 320 C and hot wire temperatures of 1035 C are typically used.

Species	Abundance	Separation Factor (α)
$^{16}O^{16}O$	99.518%	----------
$^{16}O^{18}O$	0.188%	1.006
$^{16}O^{17}O$	0.037%	1.0032
$^{18}O^{18}O$	3.57 ppm	?
$^{17}O^{18}O$	0.7 ppm	?
$^{17}O^{17}O$	0.14 ppm	?

Large separations are possible in a few meters length, but the amount of material produced per unit time is small. Thermal diffusion usually produces small quantities of highly enriched isotopes from already enriched feed stock. It requires a low capital investment, simple equipment and minimal operating costs.

2. Equipment

- a long straight tube with an external cooling jacket and an internal heated wire.
- the system must be as vertical as possible and the wire completely concentric throughout the length.
- multiple columns are usually used and some form of pump or thermal siphon is needed to transfer gas.

3. Feed stock

O_2 gas

4. Product

Enriched oxygen gas which could be marketed as is or converted to water.

5. Other chemicals

none

6. Difficulty / complexity

Thermal diffusion systems are simple to operate. Construction is difficult because the tube must be straight and the hot wire kept concentric as it warms up. Keeping the wire concentric and taut requires complicated electrical connections to allow for thermal expansion.

7. Reliability / scale / external experience

- considerable experience in isotope separation using thermal diffusion of gases.
- a lot of work has been done on oxygen.
- the Weizmann Institute, Mound, and Oak Ridge have used this system to enrich oxygen isotopes, particularly ^{17}O. These systems are usually installed as the final stages of enrichment after a process such as water distillation.
- production rates from thermal diffusion plants are small - - a few millilitres of gas per day.

8. Internal experience

none

9. Size

Thermal diffusion systems can be cascaded to form large systems

10. Analysis systems

mass spectrometric analysis of oxygen for ^{18}O or ^{17}O.

11. Waste disposal

none

12. Safety

minor safety hazard in handling gaseous oxygen at atmospheric pressure

13. Interest at Hydro

Research Division is interested in this promising technique.

14. Other notes

Probably the best system for enriching ^{17}O. It requires a feed of enriched oxygen (Weizmann Institute uses 20% ^{17}O).

References

1. Wolf D., Cohen H., "Process Design Considerations and Steady-State Operation Data for the Separation of Isotopes of Oxygen", Can. J. Chem. Eng., 50, 621 (1972).

2. Narten A.H., Landau L., "Separation of Oxygen-17 from Natural Oxygen in Thermal Diffusion Columns", J. Chem. Phys., 43, 751 (1965).

3. Mathur B.P., Watson W.W., "Thermal Diffusion in Isotopic $^{16}O_2$, $^{18}O_2$", J. Chem. Phys., 51, 2210 (1969).

Appendix 8.
Techniques not Fully Developed

The following methods are not listed in any order of preference. They cannot be analyzed as the other techniques because there is insufficient information available. All require a significant amount of research to develop them sufficiently to produce isotopes commercially. From current information none has any particular advantage for large scale production.

1. Laser Isotope Separation

2. Distillation of the NO/CH_4 azeotrope

3. Chemical exchange systems using carbamates and amines

4. GC separation - - selective absorption on substrates

5. Magnetic Isotope Separation

6. Thermal diffusion of CO

Some of these techniques show promise as methods for difficult isotopes such as ^{17}O. Laser isotope separation, in particular, has the best potential for picking out such "middle" isotopes. However, more research is necessary to develop this technique beyond the laboratory stage.

Appendix 9.
Operation of the F2 Finishing Unit at BHWP

Operation of the F2 unit at Bruce has demonstrated enrichment of ^{18}O to approximately 1.26 atom%. However, there are drawbacks in using this equipment to produce highly enriched oxygen. With an inventory of 20 Mg, the system requires a long time to reach equilibrium (>60 days for 1.26%). It has demonstrated approximately 400 theoretical plates of separation, which is insufficient to enrich ^{18}O beyond 2 - 5 atom%. The unit was designed to produce D_2O, for which the separation constant is better and for which the feed concentration from the H_2S exchange system is ≈30% not <1%.

Under ideal conditions -- running with a continuous feed of high isotopic heavy water (~0.344% ^{18}O), and withdrawing waste continuously at the top of the column -- the concentration of ^{18}O at the bottom of the tower would increase to ≈3% $D_2{}^{18}O$. This concentration of water could then be produced in large quantities as long as the feed was maintained.

Using heavy water as a feed is expensive; light water, however, is more economical. A rough calculation indicates a final concentration of ≈1.6% ^{18}O if light water is used. It is not possible to obtain a much higher concentration because of the small number of enriching stages available.